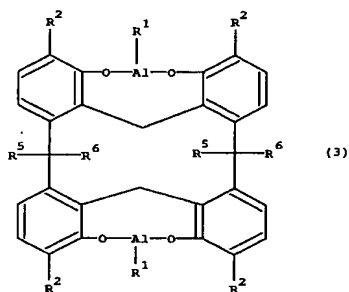


<p>2000-298580/26 A21 KAGA- 1998.09.11 ZH KAGAKU GIJUTSU SENRYAKU SUISHIN KIKO *JP 2000086755-A 1998.09.11 1998-257851(+1998JP-257851) (2000.03.28) C08G 65/10 Polymerisation catalyst compositions for propylene oxide - capable of giving hydroxyl group-terminated poly(propylene oxide) with a controlled molecular weight and a narrow distribution of the weight. C2000-090548</p>	<p>A(2-A4, 5-H4, 10-D3)</p>
<p>NOVELTY A polymerization catalyst composition comprises a crown ether compound, an alkoxide of an alkali metal or an alkali metal hydroxide and an organic Lewis acid.</p> <p>DETAILED DESCRIPTION An INDEPENDENT CLAIM is also included for a manufacturing method of poly(propylene oxide) using the polymerization catalyst compositions.</p> <p>USE The polymerization catalyst composition are useful for polymerizing propylene oxide.</p>	<p>ADVANTAGE The polymerisation catalyst composition and the manufacturing method can give hydroxyl group-terminated poly(propylene oxide) with a controlled molecular weight and a narrow distribution of the weight</p> <p>ORGANIC CHEMISTRY Preferred amounts and materials: The catalyst composition uses at least 1 mol of the crown ether compound per 1 mol of the alkali metal alkoxide or alkali metal hydroxide. The crown ether is typically of at least one of 18-crown-6, benzo-18-crown-6, benzo-18-crown-6 and dicyclohexano-18-crown-6 and the Lewis acid of at least one of methylaluminum 2,6-di-t-butyl-4-methylphenoxide, methylaluminum 2,2'-methylenebis(6-t-butyl-4-methylphenoxide) and (3). Formula (3):</p> <p>JP 2000086755-A+</p>



R¹, R⁵, R⁶ = methyl;
R² = t-butyl.

EXAMPLE

Potassium t-butoxide (0.1 mmol) was added to solution of 18-crown-6 (0.2 mmol) in methylene chloride (1 ml), 0.08 mol/l methylaluminum 2,2-methylenebis(6-t-butyl-4-methylphenoxide) methylene chloride solution (5 ml) was added to the mixed solution, propylene oxide (10 mmol) was added to the mixed solution and the

obtained mixture was stirred for 48 hours at room temperature to polymerise, giving a polypropylene oxide with a weight average molecular weight/number average molecular weight(Mw/Mn) of 1.13 in yield of 100%.
(6pp169DwgNo.0/0)

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PATENT ABSTRACTS OF JAPAN

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(54) CATALYST COMPOSITION FOR POLYMERIZING PROPYLENE OXIDE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition capable of producing poly(propylene oxide) whose mol.wt. can be controlled and which has a relatively narrow mol.wt. distribution width and hydroxyl groups at both the molecular ends by mixing a crown ether compound with an alkali metal alkoxide, etc.

SOLUTION: This catalyst composition for polymerizing propylene oxide comprises (A) a crown ether compound, preferably 18-crown 5, benzo 18-crown 6, dibenzo 18-crown 6, etc., (B) an alkali metal alkoxide such as potassium t-butoxide or an alkali metal hydroxide such as potassium hydroxide, and (C) an organic Lewis acid, preferably methyl aluminum 2,6-di-t-butyl-4- methylphenoxide, methyl aluminum 2,2'-methylenebis(5-t-butyl-4- methylphenoxide), etc. The component A is preferably contained in an amount of 1 mole per mole of the component B.

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CLAIMS

[Claim(s)]

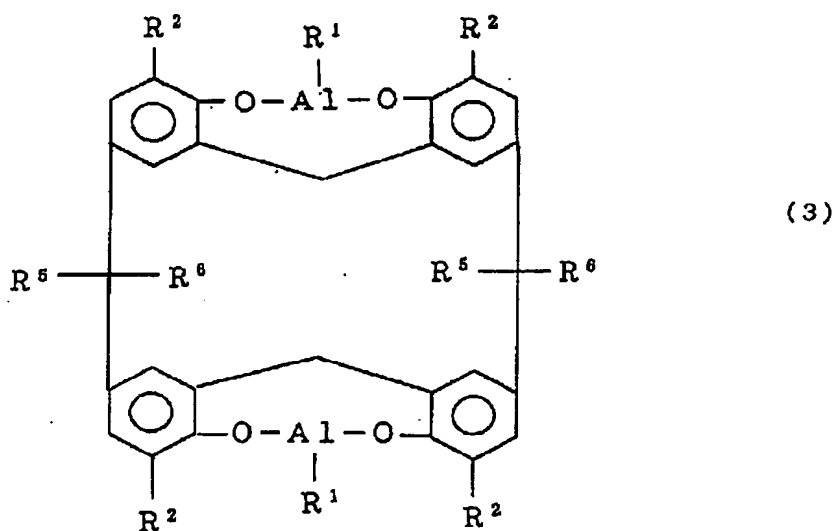
[Claim 1] The alkoxide of a crown-ether compound and alkali metal or an alkali-metal hydroxide, and the polymerization-catalyst constituent of a propylene oxide that consists of an organic Lewis acid.

[Claim 2] The catalyst constituent according to claim 1 with which one mol or more of crown-ether compounds are used to an alkali-metal alkoxide or one mol of alkali-metal hydroxides.

[Claim 3] The polymerization-catalyst constituent of the propylene oxide according to claim 1 or 2 whose crown ether is a kind chosen from the group which consists of 18-crown 6, benzo 18-crown 6, dibenzo 18-crown 6, and dicyclohexano-18-crown-6, or two sorts or more.

[Claim 4] an organic Lewis acid -- methyl aluminum 2, a 6-G t-butyl-4-methyl phenoxide, methyl aluminum 2, a 2'-methylene screw (6-t-butyl-4-methyl phenoxide), and the following formula (3)

[Formula 1]



It is the polymerization-catalyst constituent of a propylene oxide given in any 1 term of the claims 1-3 which are a kind chosen from the group which consists of (here, a methyl group and R2 are t-butyls as for R1, R5, and R6), or two sorts or more.

[Claim 5] The poly (propylene oxide) manufacture method characterized by facing carrying out the polymerization of the propylene oxide and obtaining poly (propylene oxide), and using the polymerization-catalyst constituent of a publication for a claim 1 or any 1 term of 4 as a catalyst constituent.

[Claim 6] It is the poly (propylene oxide) manufacture method according to claim 5 of being 0.01-0.15 mols preferably, on the basis of organic-metal atoms, such as aluminum by which the amount of the organic Lewis acid used is contained in an organic Lewis acid to one mol of propylene oxides, or boron.

[Claim 7] The poly (propylene oxide) manufacture method according to claim 5 or 6 which exceeds zero mol and uses a propylene oxide in the amount of 300 mols or less to the one mol of the amount of an alkali-metal alkoxide or the alkali-metal hydroxide used.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the polymerization-catalyst constituent of a propylene oxide, and the poly (propylene oxide) manufacture method. It is related with the polymerization-catalyst constituent of a propylene oxide and the poly (propylene oxide) manufacture method of manufacturing poly (propylene oxide) which has sharp molecular weight distribution in more detail.

[0002]

[Description of the Prior Art] Even if it polymerization-makes the polymerization of the propylene oxide hard to carry out as compared with ethylene oxide, the molecular weight distribution of product polymer are broadcloth in many cases, and cannot control molecular weight further easily, either. Then, research is advanced focusing on the initiator and the catalyst to obtain the polymer of narrow molecular weight distribution moreover, controlling the molecular weight of the polymer obtained.

[0003] By the method using a Lewis acid and a phosphonium halogenide, there is a report to which the polymerization of the propylene oxide could be carried out until now. However, by this method, the polymer which has a hydroxyl group at the end cannot be obtained, and it may not be suitable for a resin raw material. Moreover, there is a report to which the polymerization of the propylene oxide could be carried out by the method using an aluminum porphyrin. However, by this method, in order to use the aluminum porphyrin which it is comparatively expensive and is hard to come to hand in large quantities, there was a field it cannot be said that is industrial. Then, it also waited the deer with the narrow molecular-weight-distribution width of face of a product for development of the practical manufacture method on industry, controlling the molecular weight of the product obtained.

[0004]

[Problem(s) to be Solved by the Invention] The purpose of this invention can control the molecular weight of polymer, and is to offer the manufacture method using the polymerization-catalyst constituent which can generate poly (propylene oxide) which has a hydroxyl group at the end by moreover comparatively narrow molecular-weight-distribution width of face, and its polymerization-catalyst constituent.

[0005]

[Means for Solving the Problem] When this invention persons faced carrying out the polymerization of the propylene oxide and obtaining poly (propylene oxide), as a result of inquiring wholeheartedly that the above-mentioned technical problem should be solved and the specific polymerization-catalyst constituent was used, the polymerization of a propylene oxide is made very good, moreover, the molecular weight distribution are very sharp, they find out that the molecular weight of the polymer obtained is controllable, and came to complete this invention.

[0006] That is, this invention offers the alkoxide of a crown-ether compound and alkali metal or an alkali-metal hydroxide, and the polymerization-catalyst constituent of a propylene oxide that consists of an organic Lewis acid. Moreover, the alkoxide of a crown-ether compound and alkali metal or an alkali-metal hydroxide, and the polymerization-catalyst constituent that consists of an organic Lewis acid are used for this invention as a catalyst system, and it offers the poly (propylene oxide) manufacture method to which the polymerization of the propylene oxide is carried out.

[0007]

[Embodiments of the Invention] In this invention, a crown-ether compound, an alkali-metal alkoxide or an alkali-metal hydroxide, and three components of a specific organic Lewis acid are used as a catalyst component on the occasion of the polymerization of a propylene oxide.

[0008] A crown-ether compound will not be limited, especially if are an annular polyether, the

whole ring serves as a multidentate ligand by electron-donative oxygen, it has the function to incorporate the ion of alkali metal in hole of the ether ring of a compound and it has such a function. As these compounds, 18-crown 6, benzo 18-crown 6, benzo 15-crown 5, dibenzo 18-crown 6, dibenzo 18-crown 3, dibenzo 24-crown 8, dibenzo 30-crown 10, dicyclohexano-18-crown-6, dicyclohexano-24-crown-8, etc. can be raised. Also in these, they are 18-crown 6, benzo 18-crown 6, dibenzo 18-crown 6, and dicyclohexano-18-crown-6. It can use preferably.

[0009] Especially an alkali-metal alkoxide can be used without being limited. For example, alkoxides, such as a methoxide of alkali metal, such as caesium, a rubidium, a potassium, sodium, and a lithium, ethoxide, propoxide, and butoxide, can be raised. Also in these, it is a potassium. t-butoxide can use preferably especially.

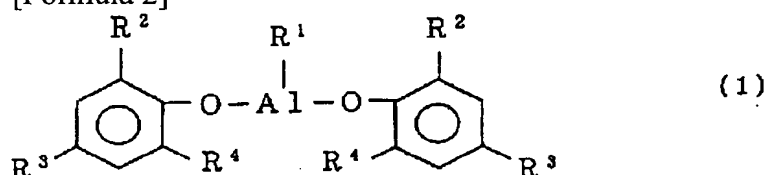
[0010] An alkali-metal hydroxide can also be used without being limited especially. For example, a lithium hydroxide, a sodium hydroxide, a potassium hydroxide, a cesium hydroxide, a hydroxylation rubidium, etc. can be raised. Also in these, a potassium hydroxide can use preferably especially.

[0011] the aforementioned specific organic Lewis acid -- the so-called "*** -- it is called high Lewis-acid" and the organic metal which has a ligand, and the Lewis acid to which the environment where are aluminum or the compound complex of boron preferably, and it has steric hindrance by this ligand is given by organic metals, such as aluminum or a boron atom, are said (In addition, as far as it is related with an organic Lewis acid in this specification, a "metal" is caught in a wide sense and boron is also described as a metal.)

The aforementioned ligand can be the shape of a chain and the annular thing which can have branching, and can be t-butyl, phenyl groups, and those derivatives. As such a compound, it is the alkylaluminum screw (alkyl phenoxide) expressed with the following formula (1), for example.

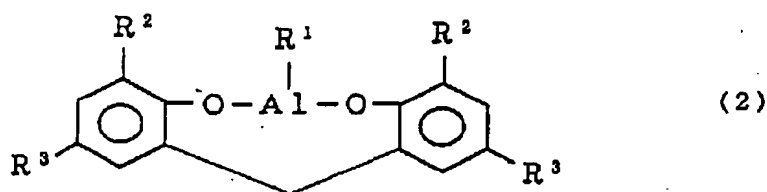
[0012]

[Formula 2]



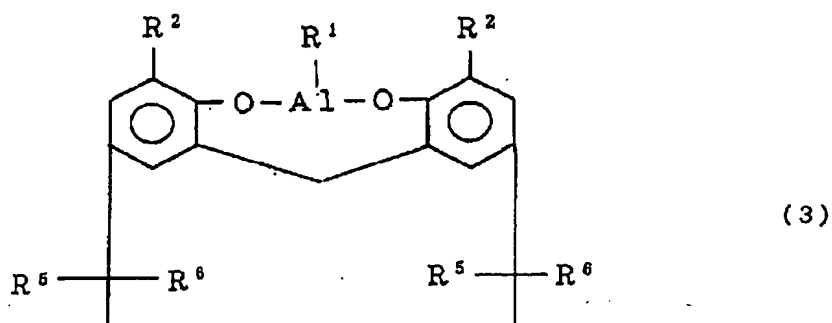
[0013] They are (R1 is a methyl group or an ethyl group among a formula, and R2, R3, and R4 express independently the alkyl group or hydrogen atom of C1-C10, respectively), and the alkylaluminum alkylene screw (alkyl phenoxide) expressed with the following formula (2). [0014]

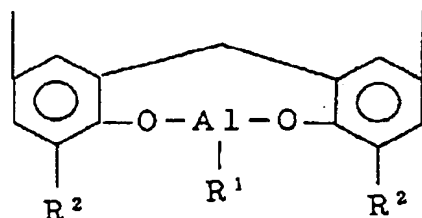
[Formula 3]



[0015] They are (R1 is a methyl group or an ethyl group among a formula, and R2 and R3 express independently the alkyl group or hydrogen atom of C1-C10, respectively), and the compound expressed with the following formula (3). [0016]

[Formula 4]





[0017] (R1 being a methyl group or an ethyl group among a formula, and R2, R5, and R6 expressing independently an alkyl group or hydrogen atom of C1-C10, respectively) and triphenyl aluminum, triphenyl boron, TORI (pentafluorophenyl) boron, etc. are raised.

[0018] In addition, in the organic metal of such an organic Lewis acid, aluminum is the most desirable and the poly (propylene oxide) polymerization degree from which boron is obtained as compared with aluminum falls a little. For example, generally the aforementioned ligand shows molecular weight distribution with the sharp (the one where a bulky difference is larger) one where the molecular weight is larger. For example, when tree i-butyl aluminum is used, there is an inclination for molecular weight distribution to become broadcloth as compared with methyl aluminum 2 and 2-methylene screw (6-t-butyl-4-methyl phenoxide). (However, it is cheap.) Also in these, methyl aluminum 2, a 6-G t-butyl-4-methyl phenoxide (CAS registration number 56252-55-2), Methyl aluminum 2, a 2'-methylene screw (6-t-butyl-4-methyl phenoxide) (CAS registration number 194997-60-9), And in the aforementioned formula (3), the compound a methyl group and whose R2 R1, R5, and R6 are t-butyls can use preferably.

[0019] The polymerization of the propylene oxide using the catalyst for polymerizations of this invention can be performed by the same method as the case where other well-known catalysts for polymerizations are used. For example, a crown-ether compound is dissolved in a suitable solvent, and the alkoxide of alkali metal is added and is made to react. Subsequently, the polymerization of the propylene oxide of an initial complement is added and carried out to the solution which added and obtained the organic Lewis acid further. One mols or more of crown-ether compounds used for this invention are used to an alkali-metal alkoxide or one mol of alkali-metal hydroxides. Since a reaction rate falls in less than one mol, it is not desirable.

[0020] One mols or more of organic Lewis acids used for this invention are used to an alkali-metal hydroxide or one mol of alkali-metal alkoxides. A reaction does not progress in less than one mol. In one mols or more, the polymerization reaction of a propylene oxide becomes quick, so that many. Moreover, the 0.01-0.15 mols of the 0.02-0.08 mols of the amount of the organic Lewis acid used to a propylene oxide are 0.04-0.05 mols especially preferably still more preferably preferably on the basis of organic-metal atoms, such as aluminum contained in an organic Lewis acid to one mol of propylene oxides, or boron. There is an inclination for a reaction rate to become it slow that it is less than 0.02 mols, and a reaction may be unable to progress easily in less than 0.01 mols.

[0021] Although this mechanism is not clear, when a crown-ether compound carries out the inclusion of the alkali-metal ion, it thinks for polymerization reaction to begin smoothly. Therefore, the poly (propylene oxide) molecular weight obtained is controllable by adjusting the mole ratio of an alkali-metal alkoxide, or an alkali-metal hydroxide and a propylene oxide. Although it should just choose the suitable range with the poly (propylene oxide) molecular weight made into the purpose, generally, to an alkali-metal alkoxide or one mol of alkali-metal hydroxides, the mole ratio of the alkali-metal alkoxide or alkali-metal hydroxide used for this polymerization reaction, and a propylene oxide exceeds zero mol, and 300 mols or less, a propylene oxide exceeds zero mol preferably and performs it in 200 mols or less. Poly (propylene oxide) of large molecular weight can be obtained as the rate of a propyne oxide is enlarged.

[0022] The well-known thing used for the polymerization of a propylene oxide can be used for the solvent used for this invention. For example, they can be ether, aliphatic hydrocarbon, aromatic hydrocarbons, halogen system solvents (methylene chloride etc.), and ketones. Especially if reaction temperature is general temperature, it cannot be limited, but it can be the same temperature requirement as the case of the polymerization of the conventional propylene oxide. However, 0-50 degrees C is desirable.

[0023] Moreover, arbitrary well-known additives can be used for the polymerization-catalyst constituent of this invention in the range which does not check a reaction. Poly (propylene oxide) obtained by this invention is applicable to various uses. For example, it can use as adhesives, an urethane raw material and a resin raw material, a surfactant raw material, etc.

[0024]

[Example] Although an example is given and this invention is explained further hereafter, please

understand that this invention is not the thing which it comes to limit to the following examples unless the summary is exceeded. In addition, the "section" in an example and "%" are based on weight criteria. Moreover, the reaction was performed under inert gas and non-water atmosphere. The molecular weight and molecular weight distribution [Mw (weight average molecular weight)/Mn (number average molecular weight)] of a product were measured by GPC (for tetrahydro furans), and computed the yield of a reaction from the result of ¹H-NMR. [0025] 0.2mmol(s) of example 1:18-crown-6 were melted to 1ml of methylene chlorides, and potassium-t-butoxide 0.1mmol was added, and concentration added 5ml (** considering as an organic high Lewis acid 0.4mmol(s)) for the methyl aluminum 2 of 0.08 mol/l, and the methylene-chloride solution of 2-methylene pith (6-t-butyl-4-methyl phenoxide). Next, the propylene oxide was added 10 mmols, and the polymerization of the 48-hour stirring was continued and carried out at the room temperature. It was 100%, when a part of this resultant was sampled and it asked for the yield of a polypropylene oxide by ¹H-NMR. Moreover, it was Mn=3900 and Mw/Mn=1.13, when added methano 1 RU of optimum dose to the sampled resultant, it was evaporated, the generated polypropylene oxide was remelted to THF and molecular weight and molecular weight distribution were measured by the filtration back GPC with the Teflon filter.

[0026] Example 2: The amount of the propylene oxide to add was set to 20mmol(s) of double precision, except it, it was operated with the same conditions as an example 1, and polymerization reaction of a propylene oxide was performed. The yield of the obtained polypropylene oxide was 100%, and was Mn=7500 and Mw/Mn=1.15. Thus, when the amount of the propylene oxide to be used was made into double precision to potassium-t-butoxide, the molecular weight of the obtained polypropylene oxide increased twice [about], with the narrow distribution maintained. It turns out at least even in molecular weight 7500 that the molecular weight of a polypropylene oxide is controllable.

[0027] 0.2mmol(s) of example 3:18-crown-6 were melted to 5ml of methylene chlorides, and potassium-t-butoxide 0.1mmol was added, and concentration added 0.4ml (referred to as aluminum (i-Bu)₃ 0.4mmol(s)) for the Korean geisha solution to the tree i-butyl aluminum's of 1.0 mol/l. Next, the propylene oxide was added 10 mmols, and the polymerization of the 48-hour stirring was continued and carried out at the room temperature. It was 100%, when a part of this resultant was sampled and it asked for the yield of a polypropylene oxide by ¹H-NMR. Moreover, it was Mn=4700 and Mw/Mn=1.65, when added the methanol of optimum dose to the sampled resultant, it was evaporated, the generated polypropylene oxide was remelted to THF and molecular weight and molecular weight distribution were measured by the filtration back GPC with the Teflon filter.

[0028] 0.2mmol(s) of example 4:18-crown -6 were melted to chlorination METEREN 5ml, and potassium-t-butoxide 0.1mmol was added, and concentration added 2ml (referred to as aluminum (i-Bu)₃ 2mmol(s)) for the hexane solution of the tree i-butyl aluminum of 1 mol/l. Next, the propylene oxide was added 100 mmols, and the polymerization of the 48:00 question stirring was continued and carried out at the room temperature. It was 100%, when a part of this resultant was sampled and it asked for the yield of a polypropylene oxide by ¹H-NMR. Moreover, it was Mn=8100 and Mw/Mn=2.13, when added the methanol of optimum dose to the sampled resultant, it was evaporated, the generated polypropylene oxide was remelted to THF and molecular weight and molecular weight distribution were measured by the filtration back GPC with the Teflon filter.

[0029] Example 5: Potassium-hydroxide 2mmol, 2mmol(s) of 18-crown -6, and tree i-butyl aluminum (aluminum₃ (i-Bu)) 4mmol were melted to THF, and volume was set to 20ml. That is, concentration of potassium ion (K⁺) was made into 0.1 mol/l. Next, 1ml was taken for this solution (for KOH, 0.1mmol(s) and 18-crown -6 are [0.1mmol(s) and aluminum (i-Bu)₃ of the amount of each component in a solution] 0.2mmol(s).), and 2mmol(s) (2ml as a hexane solution of 1 mol/l) were added for aluminum (i-Bu)₃ there. And 10ml of chlorination METEREN was added, it was diluted, the propylene oxide was added 100 mmols, and the polymerization of the 48-hour stirring was continued and carried out at the room temperature. It was 100%, when a part of this resultant was sampled and it asked for the yield of a polypropylene oxide by ¹H-NMR. Moreover, it was Mn=6200 and Mw/Mn=1.83, when added methano 1 RU of optimum dose to the sampled resultant, it was evaporated, the generated polypropylene oxide was remelted to THF and molecular weight and molecular weight distribution were measured by the filtration back GPC with the Teflon filter.

[0030] Example 6: Potassium-hydroxide 2mmol, 2mmol(s) of 18-crown -6, and triphenyl boron (BPh₃) 5mmol were melted to 5ml of methylene chlorides. The propylene oxide was added there 100 mmols, and the polymerization of the 48:00 question stirring was continued and carried out at the room temperature. It was 100%, when a part of this resultant was sampled and it asked for

yield by $^1\text{H-NMR}$. Moreover, it was $M_n=1600$ and $M_w/M_n=1.22$, when added ME evening Norian of optimum dose to the sampled resultant, it was evaporated, the generated polypropylene oxide was remelted to THF and molecular weight and molecular weight distribution were measured by the filtration back GPC with the Teflon filter.

[0031]

[Effect of the Invention] According to this invention, the molecular weight of polymer can be controlled and the manufacture method using the polymerization-catalyst constituent which can generate poly (propylene oxide) which has a hydroxyl group at the end by moreover comparatively narrow molecular-weight-distribution width of face, and its polymerization-catalyst constituent is offered.

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